

TiO₂ coated Si nanowire electrodes for electrochemical double layer capacitors in room temperature ionic liquid

Konstantinou, F.; Shougee, A.; Albrecht, T.; Fobelets, K.

DOI:

[10.1088/1361-6463/aa8717](https://doi.org/10.1088/1361-6463/aa8717)

License:

Creative Commons: Attribution (CC BY)

Document Version

Publisher's PDF, also known as Version of record

Citation for published version (Harvard):

Konstantinou, F, Shougee, A, Albrecht, T & Fobelets, K 2017, 'TiO₂ coated Si nanowire electrodes for electrochemical double layer capacitors in room temperature ionic liquid', *Journal of Physics D: Applied Physics*, vol. 50, no. 41, 415503. <https://doi.org/10.1088/1361-6463/aa8717>

[Link to publication on Research at Birmingham portal](#)

General rights

Unless a licence is specified above, all rights (including copyright and moral rights) in this document are retained by the authors and/or the copyright holders. The express permission of the copyright holder must be obtained for any use of this material other than for purposes permitted by law.

- Users may freely distribute the URL that is used to identify this publication.
- Users may download and/or print one copy of the publication from the University of Birmingham research portal for the purpose of private study or non-commercial research.
- User may use extracts from the document in line with the concept of 'fair dealing' under the Copyright, Designs and Patents Act 1988 (?)
- Users may not further distribute the material nor use it for the purposes of commercial gain.

Where a licence is displayed above, please note the terms and conditions of the licence govern your use of this document.

When citing, please reference the published version.

Take down policy

While the University of Birmingham exercises care and attention in making items available there are rare occasions when an item has been uploaded in error or has been deemed to be commercially or otherwise sensitive.

If you believe that this is the case for this document, please contact UBIRA@lists.bham.ac.uk providing details and we will remove access to the work immediately and investigate.

PAPER • OPEN ACCESS

TiO₂ coated Si nanowire electrodes for electrochemical double layer capacitors in room temperature ionic liquid

To cite this article: F Konstantinou *et al* 2017 *J. Phys. D: Appl. Phys.* **50** 415503

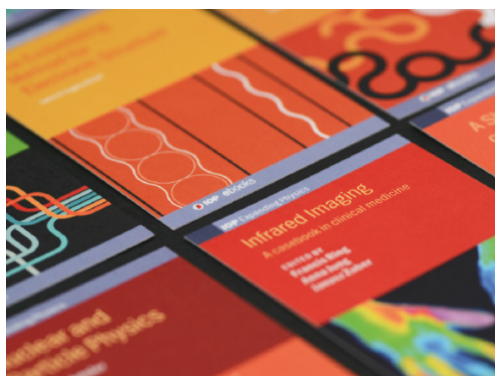
View the [article online](#) for updates and enhancements.

Related content

- [One-step synthesis of TiO₂ nanorod arrays on Ti foil for supercapacitor application](#)
Zhi Zheng, Jiajun Chen, Ryuji Yoshida *et al.*
- [Fabrication and performance evaluation of hybrid supercapacitor electrodes based on carbon nanotubes and sputtered TiO₂](#)
L S Aravinda, K K Nagaraja, H S Nagaraja *et al.*
- [MnO₂ nanorods/SiO₂ sphere coated on single-wall carbon nanotubes as supercapacitor electrode for high energy storage applications](#)
Zaharaddeen S Iro, C Subramani, T Kesavan *et al.*

Recent citations

- [Silicon-MnO₂ core-shell nanowires as electrodes for micro-supercapacitor application](#)
Ankur Soam *et al*
- [High performance silicon nanowires/ruthenium nanoparticles micro-supercapacitors](#)
Yasmina Bencheikh *et al*
- [Enhanced micro-supercapacitors in aqueous electrolyte based on Si nanowires coated with TiO₂](#)
Cheng Zhang *et al*




IOP | ebooks™

Bringing together innovative digital publishing with leading authors from the global scientific community.

Start exploring the collection—download the first chapter of every title for free.

TiO₂ coated Si nanowire electrodes for electrochemical double layer capacitors in room temperature ionic liquid

F Konstantinou^{1,2}, A Shougee^{1,2}, T Albrecht¹ and K Fobelets² 

¹ Department of Chemistry, Imperial College London, Exhibition Road, SW7 2AZ London, United Kingdom

² Department of Electrical and Electronic Engineering, Imperial College London, Exhibition Road, SW7 2BT London, United Kingdom

E-mail: k.fobelets@imperial.ac.uk

Received 26 June 2017, revised 28 July 2017

Accepted for publication 18 August 2017

Published 21 September 2017



Abstract

Three TiO₂ deposition processes are used to coat the surface of Si nanowire array electrodes for electrochemical double layer capacitors in room temperature ionic liquid [Bmim][NTF₂]. The fabrication processes are based on wet chemistry only and temperature treatments are kept below 450 °C. Successful TiO₂ coatings are found to be those that are carried out at low pressure and with low TiO₂ coverage to avoid nanowires breakage. The best TiO₂ coated Si nanowire array electrode in [Bmim][NTF₂] showed energy densities of 0.9 Wh·kg⁻¹ and power densities of 2.2 kW·kg⁻¹ with a nanowire length of ~10 μm.

Keywords: silicon nanowires, TiO₂ nanoparticles, ionic liquid, supercapacitor electrode

(Some figures may appear in colour only in the online journal)

1. Introduction

Current research on electrochemical double layer capacitors (EDLCs) is focussed on increasing the electrode's effective surface area and chemical stability, with the aim to improve their storage capacity via increased energy and power densities and cycle life [1]. Carbon-based materials with high porosities offer high chemical stability and large surface areas [2–4]. Further improvement to their storage characteristics can be achieved by coating their surface with transition metal oxide nanoparticles (NPs) such as RuO₂, NiO, MnO₂, V₂O₅, Co₂O₃, TiO₂, SnO₂, Fe₂O₃, and Fe₃O₄ [2–9]. The synergy of efficient electrical transport in the carbon and the increased surface area and/or faradaic charge storage ability of the NP coatings make composites of these materials attractive candidates for improved electrode performance in EDLCs.

An alternative approach to the use of carbon is silicon. Although Si is not as chemically inert as carbon materials, its ubiquitous nature in microelectronics makes studies on Si-based EDLCs attractive. Si-based energy storage devices can be monolithically integrated in e.g. Si-based power management systems opening up fabrication opportunities in the back-end of the Si CMOS (complementary metal-oxide-semiconductor) process industry.

The requirements for good Si-based EDLCs are similar to carbon-based systems: a large surface area and good chemical stability. The large surface area can be obtained by nano-structuring of the Si bulk. Bottom-up and top-down techniques have been applied successfully in increasing the capacitance values of Si-based EDLCs [10, 11]. Si is relatively reactive in commonly used electrolytes, with its native oxide layer unable to provide sufficient passivation. Therefore, it is essential to provide an alternative protective coating on the Si surface that increases its chemical stability while not reducing its capacitance. Si nanowires with different coatings have been investigated, offering higher electrochemical windows (EWs) and better capacitance values [10, 12, 13]. In addition to coating the

Original content from this work may be used under the terms of the [Creative Commons Attribution 3.0 licence](https://creativecommons.org/licenses/by/3.0/). Any further distribution of this work must



maintain attribution to the author(s) and the title of the work, journal citation and DOI.

Si surface, the use of room temperature ionic liquids (RTILs) as electrolyte can also increase the stability of the system [4, 12, 14, 15]. Their appeal in electrochemical applications is due to their wide operating potential window, high chemical and electrochemical stability, wide operating temperature range, high thermal stability, negligible volatility, non-flammability and relative environmental friendliness. Challenges, on the other hand, include their hygroscopicity (dissolved water reduces the potential operating window) and comparatively high viscosity (increasing the solution resistivity).

Research on alternative electrode materials, such as MWCNTs, has shown improvements of the electrode performance with TiO₂ NP coatings [16–18]. Therefore, we explore TiO₂ coated Si nanowire array (NWA) electrodes in this work.

In the fabrication process, the use of vacuum technology is avoided in preference of wet chemistry for ease of application and cost competitiveness, and temperatures are kept below 450 °C. The Si nanowire fabrication process is based on metal-assisted electrochemical etching (MACE) using AgNO₃ for the Ag NP nucleation process [19, 20]. The use of the low temperature, wet chemical process together with TiO₂ NPs coatings which are low cost, environmentally friendly and available in abundance, makes the Si-based electrode a green energy candidate.

In this work, we present three different TiO₂ coating processes applied to p-type MACE fabricated Si NWAs in the RTIL [Bmim][NTF₂]. The capacitance of the resulting electrodes is extracted using cyclic voltammetry (CV), electrochemical impedance spectroscopy (EIS), and chronopotentiometry (CP).

2. Experiments

2.1. Preparation of the Si NWA electrode

(100) p-type silicon wafers with resistivity, $\rho = 0.01\text{--}0.02\ \Omega\ \text{cm}$ (B-doped, $N_A \sim 10^{18}\ \text{cm}^{-3}$) and 525 μm thickness were purchased from Si-Mat, Kaufering, Germany. Bulk p-Si samples measuring 2 cm \times 2 cm were cleaned by sonication in IPA for 3 min, dip rinsed in deionised (DI) water, followed by a piranha (3:1 H₂SO₄:H₂O₂) clean for 10 min, and rinsed in DI water. Si NWAs were etched using a 2-step MACE process. First, Ag NPs are nucleated in a solution of 0.005 M AgNO₃ and 5 M HF for 2 min [20]. After a DI water rinse the samples are transferred to a solution of 0.1 M H₂O₂ and 4.9 M HF and etched for 60 min. After another DI water rinse, the Ag NPs are removed in a concentrated HNO₃ mixture (1:1 v/v) with DI water for 3 min and subsequently rinsed, followed by gentle drying using a dry-air gun. The length and density of Si NWs are $\sim 10\ \mu\text{m}$ and $\sim 10^9\ \text{NWs}\cdot\text{cm}^{-2}$, respectively [10]. The average diameter of the NWs is $\sim 150\ \text{nm}$ varying between $\sim 20\ \text{nm}$ and $\sim 250\ \text{nm}$. The back of the samples is protected from etching during MACE.

The materials used for wet TiO₂ deposition are: TiCl₄·2THF (97%), Ti[OCH₂(CH₃)₂]₄ (97%) and Ti foil (0.25 mm thickness, 99.7% trace metals) from Sigma-Aldrich. Acetylacetone (99%) was purchased from Merck. H₂SO₄ (95%), H₂O₂ (30%), HF (50%), HNO₃ (68%) and HCl (37%) are from VWR International Ltd.

The Si NWAs were coated with TiO₂ using three alternative coating procedures.

- (a) TiCl₄ treatment [21]: The Si NWAs (length $\sim 15\ \mu\text{m}$) were immersed in 10 ml of 0.04 M aqueous solution of titanium (IV) chloride tetrahydrofuran complex (TiCl₄·2THF) and heated at 70 °C for 30 min in the oven. Afterwards the samples were rinsed with DI water and baked at 450 °C for 30 min. EDS analysis gives large variations of the weight percentages of Ti, O and Si across the area: 0–0.12%, 8% and 92–91.88%, respectively. No Cl signal was found.
- (b) Ti-dip process [22]: The Si NWAs (length $\sim 10\ \mu\text{m}$) were immersed in 10 ml of 0.2 M titanium (IV) isopropoxide (Ti[OCH₂(CH₃)₂]₄), 0.4 M acetylacetone and 12 M absolute ethanol solution for 15 min, followed by immersion in DI water for 5 min and baked at 450 °C for 30 min in the oven. This procedure was repeated two more times in order to achieve a more uniform coating (3 \times Ti-dip process). In a 1 dip process, EDS analysis gives weight percentages of 2%, 10% and 88% for Ti, O and Si, respectively, increasing to respectively 4.5%, 13%, 82% when the dipping process is done 3 times.
- (c) Ti autoclave [23]: The Si NWAs (length $\sim 10\ \mu\text{m}$) were immersed into 30 ml of 0.1 M HCl solution and along with 0.1 g Ti foil placed into an autoclave. The autoclave was heated at 180 °C for 4 h. Afterwards, the samples were rinsed in DI water and baked at 450 °C for 30 min.

SEM images of the TiO₂ treated Si NWAs are given in figure 1. These show wide variations in material structure as a result of the applied process.

Figure 1(a) shows the catastrophic effect of the autoclave process, resulting in dramatically shortened NWs ($\sim 3\ \mu\text{m}$) covered with a discontinuous layer of TiO₂ (see inset figure 1(a)). The sudden release of the high pressure in the autoclave at the end of the process caused the layer of TiO₂, attached to the Si NWs to fracture, breaking the Si NWs. This led to a large reduction in effective surface area. The 3 \times Ti-dip process maintained the integrity of the Si NWA better. The TiO₂ particles are not homogeneously distributed (see SEM figure 1(b)) within the NWA and some circular TiO₂ NPs (diameter $\sim 135\ \text{nm}$) appear on the surface (see inset figure 1(b)). Although the EDS shows very low density of TiO₂, the SEM shows that locally high concentrations of deposited TiO₂ can be seen covering the space in between the NWs. Figure 1(c) shows increased TiO₂ deposition using the TiCl₄ process. The Si NWA however became very brittle due to large densities of TiCl₄·2THF-related material filling the regions between the NWs in the array, which upon expansion during the thermal process puts the Si NWs under stress. There is a large size distribution of particles, with diameters measured between $\sim 40\ \text{nm}$ and $\sim 550\ \text{nm}$. Figure 1(d) gives an untreated SiNWA.

2.2. Experimental set-up for electrochemical measurements

For electrochemical measurements, the back of the Si NWA surface was plasma etched first in a mixture of Ar

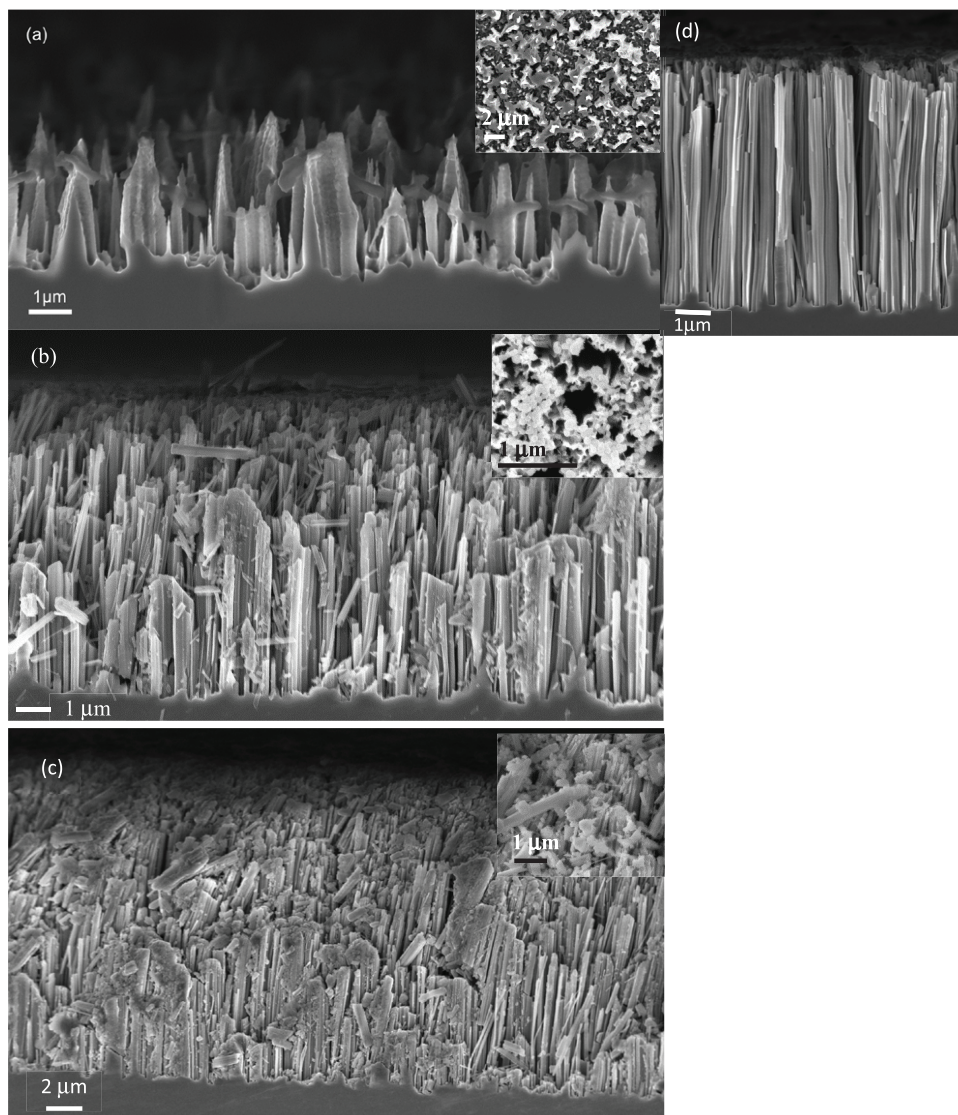


Figure 1. SEM images of the different TiO_2 treated Si NWA. (a) Si NWA sample coated in the Ti autoclave process showing the fractured NWA structure, (b) Si NWA sample coated by the $3 \times$ Ti-dip processes showing a well fabricated NWA structure (inset shows TiO_2 nano particles on the top of the NWs) and (c) TiCl_4 process showing TiO_2 coating but brittle easily broken NWs. (d) Uncoated NWs.

(25 sccm)– O_2 (10 sccm) at 200 W for 5 min at 20 °C for removal of the coating layer, followed by CHF_3 (25 sccm)–Ar (25 sccm)– O_2 (2 sccm) at 200 W for 5 min at 20 °C to remove any oxide growth. The plasma etch step is immediately followed by a ~ 100 nm Al deposition using thermal evaporation. The back contacts were annealed at 200 °C for 1 min under Ar atmosphere.

A 3-electrode setup is used, with the Si NWA as the working electrode, a Pt coil wire as the counter electrode and an Ag wire as the pseudo-reference electrode. The electrochemical measurements were conducted in a custom-built electrochemical cell constructed of two Teflon sections that clamp the working electrode. The projected surface area, i.e. the working electrode surface area in contact with the electrolyte solution, is $A = 1.327 \text{ cm}^2$. All extracted areal capacitances presented in this work will be calculated using the projected surface area defined by the electrochemical cell.

All the electrochemical measurements were conducted with a CHI760C potentiostat. The RTIL [Bmim][NTf₂] (BASF, purity $\geq 98\%$) composed of 1-butyl-3-methylimidazolium

cations and bis(trifluoromethanesulfonyl) imide anions is used as electrolyte. The operating potential window (EW) for the quasi-rectangular shaped CVs is determined from the potential range where the maximum current $I_{\text{max}} = 3 \times i$ with i determined in the middle of the EW [10]. The EW for the CV plots with peaks is calculated from the voltage range constrained to where the maximum current $I_{\text{max}} = 3/2 (i_a + i_c)$, with $i_{a,c}$ anodic and cathodic current peak, respectively. The EW for dry ionic liquid, with a 11 ppm water content as determined by Karl–Fischer titration, using a Au electrode, Au/[Bmim][NTf₂] is 4.4 V.

3. Results and discussions

The CVs of an uncoated and a SiO_2 -coated B-doped Si NWA in [Bmim][NTf₂] are shown in figure 2(a). The thin SiO_2 coating is achieved by oxidising the Si NWA in 90 °C HNO_3 [10]. It is clear that the thin (< 2 nm) SiO_2 coating increases the EW of the system by nearly a factor of 2.

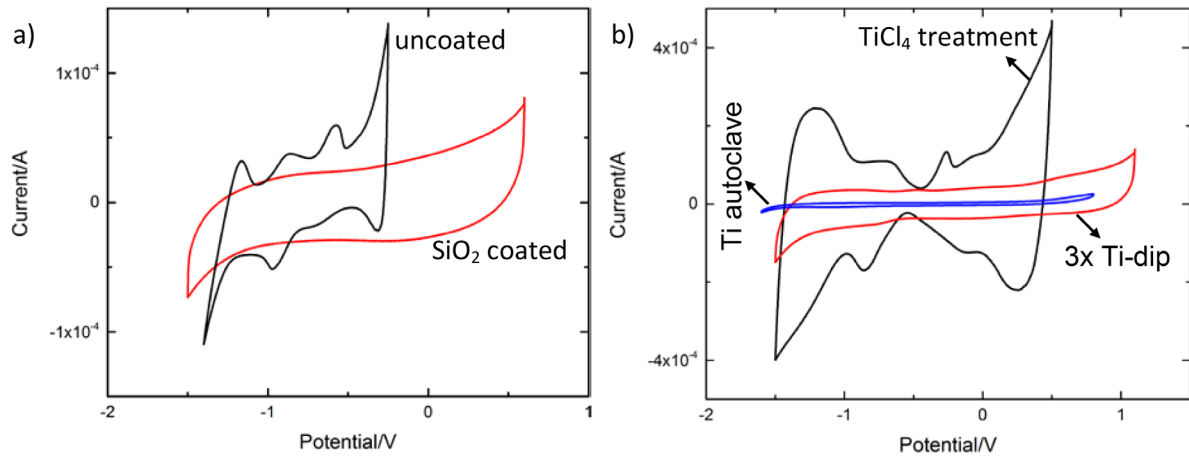


Figure 2. Cyclic voltammograms of (a) uncoated (black line) and SiO₂ coated (red line) Si NWA and (b) Si NWA coated by TiCl₄ treatment (black line), 3 × Ti-dip (red line) and Ti-autoclave (blue line), all in [Bmim][NTf₂] at scan speed, $v = 50 \text{ mV} \cdot \text{s}^{-1}$.

Figure 2(b) shows the cyclic voltammograms of the Si NWAs in [Bmim][NTf₂] coated by the three different TiO₂ coating processes. The CV of the uncoated and TiCl₄-treated Si NWA has current peaks. These are strongly correlated with the presence of NWs since no peaks are observed for bulk material in the same set-up and RTIL. Our hypothesis is that these redox peaks are related to deep level surface traps in the Si NWs created in the MACE process [24]. Although the dynamics of the charging and discharging of the traps into a thin H₂O layer surrounding the NWs adds to the overall capacitance values, measurements have demonstrated a stronger degradation of their capacitance upon repeated cycling of the capacitor. The EW, anodic current and areal capacitance for all samples are given in table 1.

The areal capacitance, C is calculated from the CV plots by:

$$C = \frac{i}{dV/dt} \cdot \frac{1}{A}, \quad (1)$$

where $i = \frac{i_a + i_p}{2}$ with $i_{a,p}$ the anodic and cathodic current, respectively defined from the voltammogram at their minimum absolute value (approximately in the middle of the CV plot), dV/dt is the experiment's scan rate and A is the projected surface area.

The variation of the extracted capacitance between the different techniques is mainly due to the additional redox reactions occurring at the surface of the Si NWs. This leads to much higher CP values than those calculated by the CV technique and to EIS values that are dependent on the bias point (here reported for $V = 0 \text{ V}$).

The small EW indicates a low electrochemical stability of the uncoated Si NWA even in RTIL. Coating the Si NWs with a thin SiO₂ layer fabricated in boiling nitric acid at 90 °C is demonstrating much improved Si NWA performance in RTIL [10]. The coating process with TiO₂ also improves the performance of the Si NWA in two cases out of three, the TiCl₄ treatment and Ti-dip process. The reduced performance of the autoclave sample is due to the very short NW lengths. The relatively large voltage window suggests good TiO₂ coverage of the Si NWs though. The capacitance of the TiCl₄-treated

Table 1. EW, current values and areal capacitance of each working electrode in [Bmim][NTf₂], extracted from the CV measurements.

Working electrode	EW (V)	Current, i (A)	Technique used ($\mu\text{F} \cdot \text{cm}^{-2}$)		
			CV	EIS	CP
uncoated	1.1	2.5×10^{-5}	145	75	155
Coated with SiO ₂	2.1	2.6×10^{-5}	192	109	193
TiCl ₄ treatment	2.0	3.2×10^{-5}	484	90	1281
3 × Ti-dip	2.6	3.7×10^{-5}	360	324	386
Ti autoclave	2.4	0.4×10^{-5}	21	15	22

sample has an EW inferior to the other processes due to the inhomogeneous coverage. The currents are higher, mainly caused by the additional redox reactions that occur at the Si NWA surface and the slightly higher NW length. In the case of 3 × Ti-dip, the highest EW and highest current i is achieved. This shows the success of the simple 3 × Ti-dip process to increase the electrochemical stability of the Si NWA it coats.

Overall, the thin TiO₂ coating has increased the electrochemical stability of the Si NWA as demonstrated by the increased EW.

For CP in a three-electrode configuration, a constant current is applied between the working and the counter electrodes and the potential of the working electrode is measured as function of time with respect to the reference electrode. The current is cycled between $7.5 \cdot 10^{-4} \text{ A}$ and $-7.5 \cdot 10^{-4} \text{ A}$ whilst the voltage is limited by the EW given by the CV measurement (see figure 3(a)). The areal capacitance is then calculated as in equation (1) with dV/dt the average slope of the potential versus time plots.

EIS measurements are carried out in a frequency range of $1 \text{ Hz} < f < 10^5 \text{ Hz}$ using an ac voltage amplitude of 5 mV at a DC voltage where the minimum absolute value of the anodic/cathodic current is found in the CV plot (see figure 3(b)). A simplified Randles circuit consisting of an electrolyte resistance (R_s) in series with the parallel connection of the double layer capacitance (C_{DL}) and the charge transfer resistance (R_{CT}), was used to fit the Nyquist plots $|Z''|$ as a function of Z' with the total impedance $Z = Z' + jZ''$.

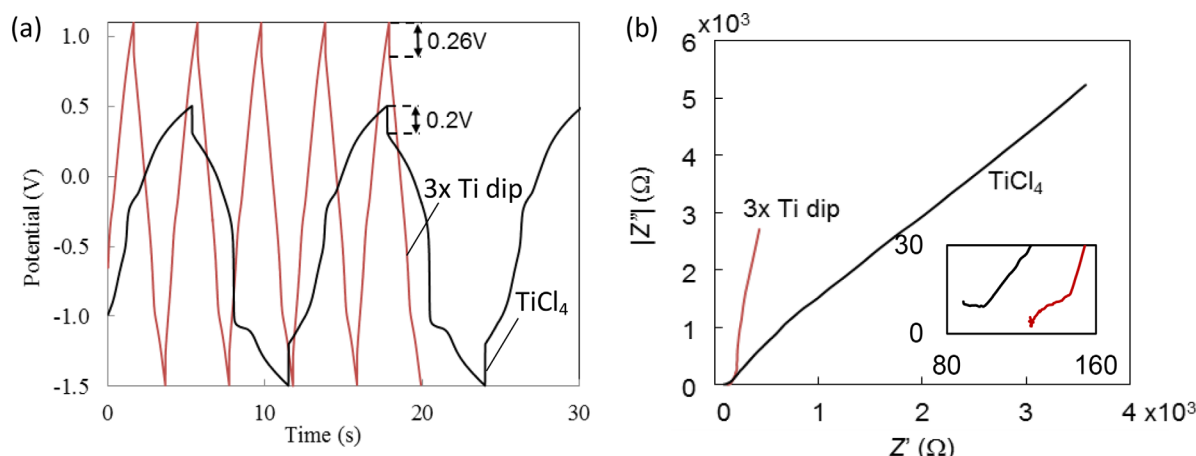


Figure 3. (a) Cyclic charge–discharge (CP) characteristics at current $i = \pm 7.5 \times 10^{-4}$ A for Ti NP coated Si NWAs. (b) EIS measurements at -0.5 V for the TiCl_4 treated sample and -0.4 V for the $3 \times$ Ti dip sample in a frequency range: $1 \text{ Hz} < f < 10^5 \text{ Hz}$. Inset: $|Z''|$ as a function of Z' in the high frequency region. Left curve is the TiCl_4 sample. (red: $3 \times$ Ti dipped sample and black TiCl_4 treated sample).

Figure 3 gives the EIS and CP plots of the $3 \times$ Ti dip and the TiCl_4 sample.

The CP plot of the $3 \times$ Ti dipped electrode shows good triangular potential variations with an ESR (equivalent series resistance) of approximately 347Ω . In contrast, the TiCl_4 treated electrode shows strong non-ideality, consistent with the strong peaks in the CV plot. Its ESR is 267Ω . The EIS measurements shown were carried out at -0.4 V for the $3 \times$ Ti dipped electrode and at -0.5 V for the TiCl_4 treated sample, the voltage where the anodic current is minimum. The resistance, $R_S + R_{CT}$ at $\omega = 10^5 \text{ Hz}$ is approximately 125 and 89Ω , respectively (see inset figure 3(b)). The high frequency inset also shows small semicircles. Since their diameter is small, the charge transfer resistance R_{CT} is small, indicating good ionic conduction and electrolyte diffusion through the nanowire structure. The slope of the straight line in the low frequency region is highest for the $3 \times$ Ti dip process indicating purer capacitive behaviour.

4. Conclusions

Si NWA electrodes were fabricated using 2-step MACE and coated with TiO_2 NPs using 3 different techniques. The length of the NWs was $\sim 10\text{--}15 \mu\text{m}$. All samples covered with TiO_2 showed improved EWs. The NW electrodes treated in the autoclave broke due to high pressure change but the $3 \times$ Ti-dip process by immersion in a $\text{Ti}[\text{OCH}_2(\text{CH}_3)_2]_4$:acetylacetone:ethanol solution was most successful. It gave the best areal capacitance of $386 \mu\text{F}\cdot\text{cm}^{-2}$ based on the CP technique. This high capacitance value is the result of the increase of the effective surface area and the larger EW due to an increase in chemical robustness. Its cyclic voltamogram did not show redox peaks, giving improved cyclability. The extracted energy density is $0.9 \text{ Wh}\cdot\text{Kg}^{-1}$ and power density is $2228 \text{ W}\cdot\text{kg}^{-1}$, placing the TiO_2 coated Si NWA using a $3 \times$ Ti dip process well within the supercapacitor range on the Ragone plot.

Acknowledgment

AS acknowledges funding from the EEE department for his PhD research. KF thanks Dr T Tate and Dr X Li for their help with EDS and the autoclave experiment, respectively.

ORCID iDs

K Fobelets  <https://orcid.org/0000-0001-5607-8243>

References

- [1] Beidaghi M and Gogotsi Y 2014 Capacitive energy storage in micro-scale devices: recent advances in design and fabrication of micro-supercapacitors *Energy Environ. Sci.* **7** 867–84
- [2] Zhai Y, Dou Y, Zhao D, Fulvio P F, Mayes R T and Dai S 2011 Carbon materials for chemical capacitive energy storage *Adv. Mater.* **23** 4828–50
- [3] Frackowiak E and Béguin F 2001 Carbon materials for the electrochemical storage of energy in capacitors *Carbon* **39** 937–50
- [4] Simon P and Gogotsi Y 2008 Materials for electrochemical capacitors *Nat. Mater.* **7** 845–54
- [5] Lee J Y, Liang K, An K H and Lee Y H 2005 Nickel oxide/carbon nanotubes nanocomposite for electrochemical capacitance *Synth. Met.* **150** 153–7
- [6] Boukhalfa S, Evanoff K and Yushin G 2012 Atomic layer deposition of vanadium oxide on carbon nanotubes for high-power supercapacitor electrodes *Energy Environ. Sci.* **5** 6872–9
- [7] Manikandan K, Dhanuskodi S, Mahesware N and Muralidharan G 2016 SnO_2 nanoparticles for supercapacitor application *AIP Conf. Proc.* **1731** 050048
- [8] Wang D, Li Y, Wang Q and Wang T 2012 Nanostructured Fe_2O_3 –graphene composite as a novel electrode material for supercapacitors *J. Solid State Electrochem.* **12** 2095–102
- [9] Eskusson J, Rauwel P, Nerut J and Jänes A 2016 A hybrid capacitor based on Fe_3O_4 –graphene nanocomposite/few-layer graphene in different aqueous electrolytes *J. Electrochem. Soc.* **163** A2768–75

- [10] Qiao L, Shougee A, Albrecht T and Fobelets K 2016 Oxide-coated silicon nanowire array capacitor electrodes in room temperature ionic liquid *Electrochim. Acta* **210** 32–7
- [11] Thissandier F, Le Comte A, Crosnier O, Gentile P, Bidan G, Hadji E, Brousse T and Sadki S 2012 Highly doped silicon nanowires based electrodes for micro-electrochemical capacitor applications *Electrochem. Commun.* **25** 109–11
- [12] Berton N, Brachet M, Thissandier F, Bideau J L, Gentile P, Bidan G, Brousse T and Sadki S 2014 Wide-voltage-window silicon nanowire electrodes for micro-supercapacitors via electrochemical surface oxidation in ionic liquid electrolyte *Electrochem. Commun.* **41** 31–4
- [13] Alper J P, Vincent M, Carraro C and Maboudian R 2012 Silicon carbide coated silicon nanowires as robust electrode material for aqueous micro-supercapacitor *Appl. Phys. Lett.* **100** 2012
- [14] Armand M, Endres F, MacFarlane D R O H and Scrosati B 2009 Ionic-liquid materials for the electrochemical challenges of the future *Nat. Mater.* **8** 621–9
- [15] McEwen A B, Ngo H L, LeCompte K and Goldman J L 1999 Electrochemical properties of imidazolium salt electrolytes for electrochemical capacitor applications *J. Electrochem. Soc.* **146** 1687–95
- [16] Jiang L-C and Zhang W-D 2009 Electrodeposition of TiO_2 nanoparticles on multiwalled carbon nanotube arrays for hydrogen peroxide sensing *Electroanalysis* **21** 988–93
- [17] Kim H-I, Kim H-J, Morita M and Park S-G 2010 Preparation and electrochemical performance of CNT electrode with deposited titanium dioxide for electrochemical capacitor *Bull. Korean Chem. Soc.* **31** 423–8
- [18] Mirmohseni A, Dorraji M S S and Hosseini M G 2012 Influence of metal oxide nanoparticles on pseudocapacitive behavior of wet-spun polyaniline-multiwall carbon nanotube fibers *Electrochim. Acta* **70** 182–92
- [19] Huang Z, Geyer N, Werner P, de Boer J and Gösele U 2011 Metal-assisted chemical etching of silicon: a review *Adv. Mater.* **23** 285–308
- [20] Xu B and Fobelets K 2014 Spin-on-doping for output power improvement of silicon nanowire array based thermoelectric power generators *J. Appl. Phys.* **115** 214306
- [21] Kumar A, Madaria A R and Zhou C 2010 Growth of aligned single-crystalline rutile TiO_2 nanowires on arbitrary substrates and their application in dye-sensitized solar cells *J. Phys. Chem. C* **114** 7787–92
- Ntais S, Dracopoulos V and Siokou A 2004 $\text{TiCl}_4(\text{THF})_2$ impregnation on a flat $\text{SiO}_2/\text{Si}(100)$ and on polycrystalline Au foil: determination of surface species using XPS *J. Mol. Catal. A* **220** 199–205
- [22] Wang X, Wu G, Zhou B and Shen J 2013 Optical constants of crystallized TiO_2 coatings prepared by sol-gel process *Materials* **6** 2819–30
- [23] Guo W, Xu C, Wang X, Wang S, Pan C, Lin C and Wang Z L 2012 Rectangular bunched rutile TiO_2 nanorod arrays grown on carbon fiber for dye-sensitized solar cells *J. Am. Chem. Soc.* **134** 4437–41
- [24] Shougee A, Konstantinou F, Albrecht T and Fobelets K 2017 Cyclic voltammetry peaks due to deep level traps in Si nanowire array electrodes in preparation